

Supporting Information

Title: Transition of Surface-Interface Creasing in Bilayer Hydrogels

Free energy density without initial swelling

The well-known free energy density due to Flory and Rehner (1943) is adopted in this study. Hong et al. (2008) formulated it as a function of the deformation gradient tensor \mathbf{F} and chemical potential μ :

$$W(\mathbf{F}, \mu) = \frac{1}{2}NkT(I_1 - 3 - 2\ln J) - \frac{kT}{\nu} \left[(J - 1) \ln \frac{J}{J-1} + \frac{\chi}{J} \right] - \frac{\mu}{\nu}(J-1) \quad (1)$$

Where $I_1 = \text{tr}(\mathbf{F}^T \mathbf{F})$, $J = \det \mathbf{F}$. The first Piola-Kirchhoff stress \mathbf{P} and the mass density of water C can be calculated as

$$\mathbf{P} = \partial_{\mathbf{F}} W = NkT(\mathbf{F} - \mathbf{F}^{-T}) + \frac{kT}{\nu} \left(\frac{1}{J} + \frac{\chi}{J^2} + \ln \frac{J-1}{J} - \frac{\mu}{kT} \right) \mathbf{J} \mathbf{F}^{-T} \quad (2)$$

$$C = -\partial_{\mu} W = \frac{J-1}{\nu} \quad (3)$$

with respect to the dry reference configuration. The product νC is the volume of solvent imbibed in the network, and it arises from the incompressibility of individual polymeric and solvent molecules, such that the volume of the hydrogel equals the sum of individual molecules of the dry network and solvent. This gives the constraint $J = 1 + \nu C$.

The parameter $N\nu$, where N is the number of network chains per unit (initial) volume and ν the volume per solvent molecule, is a measure of degree of cross-links, or cross-link density of the polymer network. kT is the absolute temperature in the unit of energy, and χ is a dimensionless measure of the enthalpy of mixing. The chemical potential μ , which is work-conjugate to C , between the external solvent and the hydrogel is set up during the migration of solvent molecules in or out of the polymer network. The potential provides the driving force for swelling or deswelling of the hydrogel.

Free energy density with initial swelling

In this paper we neglect the diffusion process and consider the steady-state where μ is prescribed by the external solvent.

As mentioned above, the free-energy density (1) takes the dry, solvent-free network as the reference state. It is numerically convenient to take a state with initial swelling as a new reference configuration. This state is characterized by isotropic stretch λ_0 , and is termed as the initial swelling ratio. At this point we introduce a parameter that is commonly used to describe the composition of hydrogels: initial polymer volume fraction ϕ_0 , defined as the ratio of volume of polymer to the volume of the initially swollen hydrogel (polymer and solvent) such that $\phi_0 = \lambda_0^{-3}$ where $0 < \phi_0 < 1$.

The initial swelling state is stress-free. Substituting $\mathbf{F} = \lambda_0 \mathbf{I}$, where \mathbf{I} is a unit tensor, $\lambda_0 = \phi_0^{-1/3}$ and $J = \phi_0^{-1}$ into (2) gives

$$\frac{\mu_0}{kT} = \frac{\mu}{kT} \Big|_{\mathbf{F}=\lambda_0 \mathbf{I}} = N\nu(\phi_0^{1/3} - \phi_0) + \phi_0 + \chi\phi_0^2 + \ln(1 - \phi_0) \quad (3)$$

With respect to the initial swelling state, difference of the free energy densities

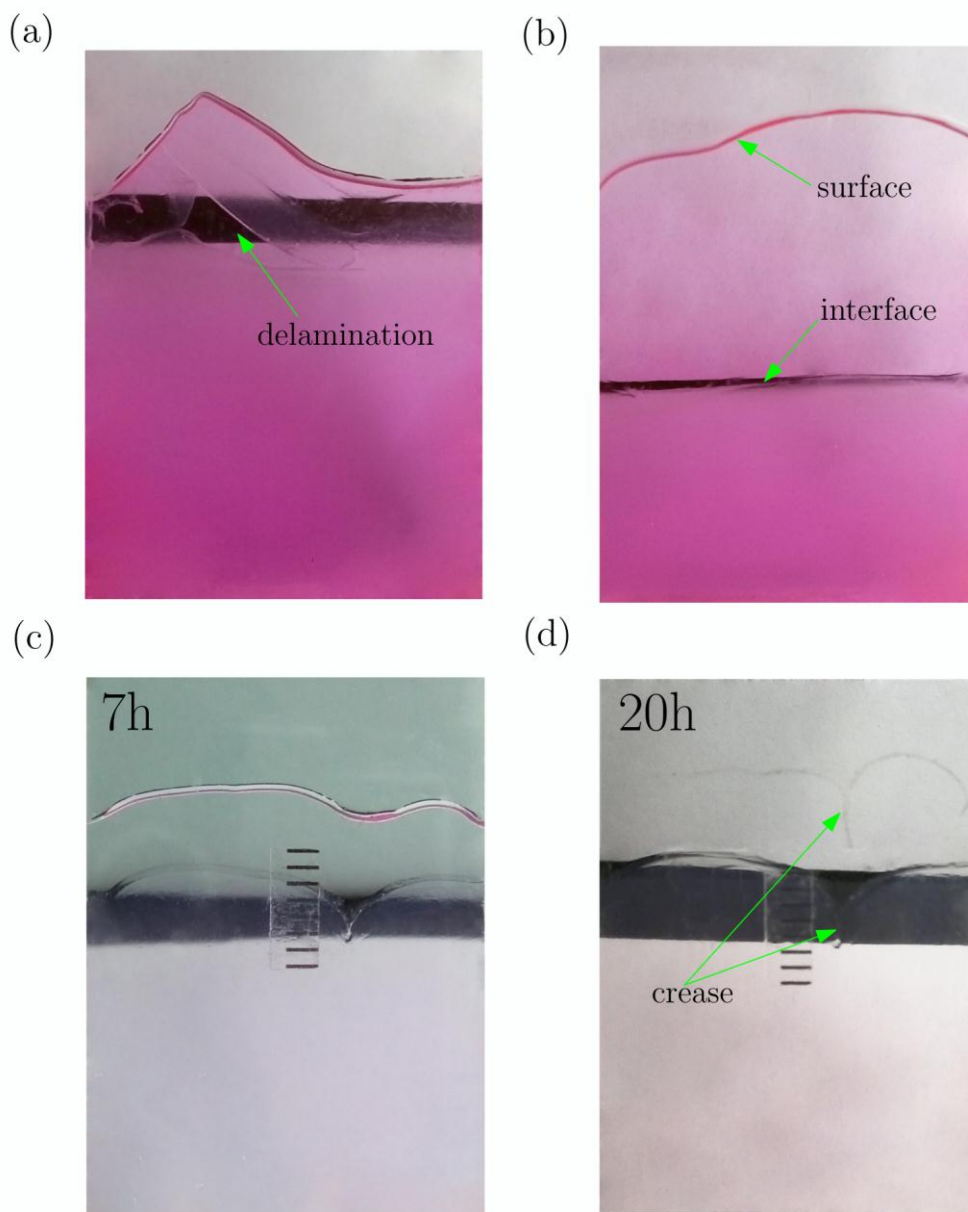
$$\begin{aligned}
\Delta W(\mathbf{F}, \Delta\mu) &= \phi_0 W(\phi_0^{-1/3} \mathbf{F}, \mu) - \phi_0 W(\phi_0^{-1/3} \mathbf{I}, \mu_0) \\
&= \frac{1}{2} NkT [\phi_0^{1/3} (I_1 - 3) - 2\phi_0 \ln J] \\
&\quad - \frac{kT}{\nu} \left[(J - \phi_0) \ln \frac{J}{J - \phi_0} - \chi \phi_0^2 \frac{J - 1}{J} + (1 - \phi_0) \ln(1 - \phi_0) \right] \\
&\quad + \frac{\mu_0}{\nu} (1 - J) - \frac{\Delta\mu}{\nu} (J - \phi_0)
\end{aligned} \tag{4}$$

defines the *effective* free energy density with initial swelling, where $\Delta\mu = \mu - \mu_0$ is the change in chemical potential with respect to the reference state of initial swelling. One can verify that $\Delta W(\mathbf{I}, 0) \equiv 0$.

Flory, P.J., Rehner, J., 1943. Statistical mechanics of cross-linked polymer networks II: Swelling. *J. Chem. Phys.* 11, 521-526.

Hong, W., Zhao, X.H., Zhou, J.X., Suo, Z.G., 2008. A theory of coupled diffusion and large deformation in polymer gels. *J. Mech. Phys. Solids* 56, 1779-1793.

Figure S1



a) The delamination of the interface for the bilayer hydrogel occasionally. Our experiments show that the bilayer gels involved in our experiments mostly are well bonded so that delamination is seldom.

b) If the friction between the glass box and the bilayer gel is not controlled well, the barreling instability can occur. Then surface crease or interface crease cannot appear.

In our experiments, we find that the interface crease may occur first and then the surface crease may appear later. c) The interface crease occurs 7 hours later after immersing the glass box with the bilayer gel into the water. d) Both interface and surface creases appear around 20 hours. The phase diagram shown in **Figure 9** only gives the condition that the surface or interface crease occurs first. The possible appearance of both surface and interface crease at the same time cannot be excluded. However, by controlling the contact time for the bilayer gel with the water, the independent surface or interface crease can be obtained.

Movie S1

After immersing the glass box with bilayer hydrogel, the expansion of the hydrogel will lead to compression in both layers. The compression will cause the nucleation and growth of surface or interface creases depending on the modulus and height ratios. (a) Surface crease; (b) Interface crease.